

Topical Report

SCREENING OF COSURFACTANT-FREE SLUGS

Project BE4A, milestone 12, FY87

By David K. Olsen

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Fred W. Burtch, Project Manager
Bartlesville Project Office
U. S. Department of Energy

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IIT Research Institute
National Institute for Petroleum and Energy Research
P. O. Box 2128
Bartlesville, Oklahoma 74005
(918) 336-2400

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ABSTRACT

This report summarizes work completed in FY86 on the "Design of Surfactant Slugs", Project BE4A, Task 1, completing milestone 12.

There are a wide variety of surfactants that show promise as not requiring a cosolvent or blend of surfactants to generate low interfacial tensions and enhance oil recovery. Three classes of compounds were considered: sodium dinonylphenoethoxy sulfonates, carboxymethylated ethoxylates, and amine oxides. The most progress on surfactant screening was made with amine oxides and carboxymethylated ethoxylates. This report describes our initial work with amine oxides as surfactants for chemical flooding. Our work on carboxymethylated ethoxylates was previously reported in NIPER-228.

Amine oxides have high salinity tolerance, generate three-phase systems over a wide salinity range, yield low interfacial tensions, have high solubilization parameters, and, at the same time, increase the viscosity of the surfactant slug without the addition of polymer, and thus avoiding problems caused by surfactant - polymer interactions. The oil displacement results reported incorporate alcohol as a cosurfactant in the amine oxide formulations, however, compounds that attempt to incorporate the cosolvent moiety into the amine oxide molecule (ethoxylated or propoxylated amine oxides) are being studied at NIPER.

OBJECTIVE

As defined in task 1, milestone 12, Project BE4A of the FY86 Annual Research Plan, NIPER-85, 12, the objective of this research was to develop surfactant slugs that maintain their integrity by use of either surfactants requiring no alcohol or surfactant-alcohol blends with properly matched partition coefficients. An alternative approach was to develop injection strategies¹ for multiple slugs that result in effective oil recovery.

The approach pursued was to design a surfactant molecule with an alcohol function (cosurfactant or cosolvent) incorporated into the molecule, thereby eliminating the requirement for surfactant-alcohol blends and/or multiple

slugs. Based upon a literature review, several surfactant systems were identified and pursued during FY86 and are reported herein. These systems included commercial surfactants from the following classes: amine oxides, ethoxylated sulfonates, and carboxymethylated ethoxylates. Our work on carboxymethylated ethoxylates was previously reported.²

INTRODUCTION

Background

Chemical flooding methods such as polymer, micellar-polymer, and alkaline flooding offer the promise of being applicable to a wide variety of reservoirs over broad ranges of conditions; that is salinities, temperatures, rock matrix, and crude oils. Chemical flooding systems, or slugs, are formulated by blending together a number of chemical components in proportions that lead to optimal oil recovery. A well-optimized chemical flooding system can recover nearly 100 percent of the oil it contacts (high local displacement efficiency). The major problems hindering the large-scale commercialization of chemical flooding technology are development of cost-effective systems that provide high sweep efficiency and maintain their effectiveness or integrity as they propagate through the reservoir.

Loss of slug integrity has been identified as the major factor in inadequate performances of many surfactant EOR field tests.³ Most of those injected formulations contained multiple surfactants, cosolvents, and alcohols and each transported through the reservoir at different rates resulting in degradation of an optimized slug within short distances from injection wells.

Separation of alcohol (cosolvent or cosurfactant) from the surfactant may result from differences in relative adsorption of the alcohol and surfactant, chromatographic separation of the surfactant-alcohol blend, or differences in the hydrophobicity of the blend, resulting in the components partitioning to different extents into the aqueous phase and oleic phase. The most promising way of avoiding slug disintegration is to design single-component slugs. In this case, the separate roles of the usual diverse components that comprised many of the early petroleum sulfonate slugs must be played by one material:

- low molecular weight surfactant -- solubilizing, water soluble
- high molecular weight surfactant -- oil moving, oil soluble
- alcoholic cosolvent -- viscosity enhancement and emulsion control.

A second approach is to use components that are matched so they will copartition. The major problem is that this matching must persist over a range of concentrations, changing oil composition and salinities as the slug moves through the reservoir. It must also be recognized that partitioning will be modified by interaction between surfactant and alcohol and by adsorption/desorption (retention) on the rock surface.

A third strategem for avoiding adverse partitioning effects would be to avoid the necessity for coherent slugs by injecting successive slugs of different composition. This concept is inspired by the demonstrated advantages in using a gradient of salinities that encompass the optimal value. An example of this approach may be injection of an alcohol-lean slug following an alcohol-rich slug that might compensate for a tendency for the alcohol to be transported faster than the surfactant. If the behavior were reversed, the injection strategy could be reversed. However, in light of the difficulty encountered in a heterogeneous reservoir of maintaining a single slug or front, the problems associated with effective design and implementation based upon the above hypothesis seem overwhelming. Prediction of front performance on sequential slugs is a common technique in high performance liquid chromatography, HPLC. Since reservoirs are neither uniform nor predictable (interwell interpretation) this approach was discouraging. One could undoubtedly formulate systems that pass one another but control of when and where and for how long both banks would coexist would be a challenge.

Application of any chemical EOR method usually requires that the chemical slug must either contain polymer or be followed by a polymer slug for mobility control. The behavior of polymer solutions, including the viscosity and viscoelasticity, is related to the ability of a polymer to provide mobility control in a chemical flood. Problems of surfactant-polymer compatibility and the compatibility of the polymer with a degraded-nonoil slug have been observed.¹ Chemical stability of both polymers and surfactants is important in designing effective chemical flooding systems because both influence all of the injection strategies listed above unless the surfactant also provides the required mobility control.

The 1984 National Petroleum Council⁴ report indicates some of the opportunities and limitations that exist for chemical flooding EOR. These constraints are emphasized in the U.S. Department of Energy analysis of EOR⁵⁻⁷

and indicates the major steps necessary to make EOR cost-effective. There are floodable reservoirs that span the entire spectrum of salinity, mineralogy, clay content, oil composition, wettability, and temperature with potentially chemically floodable recoverable oil reserves that have been defined in previous DOE and industrial publications.^{4,8-9}

ACKNOWLEDGMENTS

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LITERATURE SEARCH - COSURFACTANT FREE SLUGS

Matching the multitude of possible surfactants to the number of floodable reservoirs, each with its own temperature, brine and oil composition or range of compositions, has moved from an Edisonian approach toward a scientific approach. The first design of simplified systems uses alkanes or alkyl benzenes to model the crude oil, then once the simplified system is understood, (in whole or in part) a live crude oil at reservoir conditions is used. There seems to be no single surfactant or class of surfactants suitable for all chemically floodable reservoirs but rather a spectrum of possible compounds that could be used for any specific site (single reservoir zone, temperature, oil, and salinity, etc.).

Petroleum sulfonates have been used as the primary surfactant for most of the early enhanced oil recovery laboratory and field tests. Their low cost, however, does not overcome the chemical and physical limitations inherent in the molecules and that limit their application. Commercial petroleum sulfonates are complex mixtures and therefore are expected to chromatographically separate, and phase partition to different extents. Petroleum sulfonates have a low electrolyte tolerance that decreases with

increasing molecular weight for monosulfonate. They often require cosolvents or cosurfactants such as low-molecular-weight alcohols to generate the desired phase behavior within the reservoir and minimize the formation of macroemulsions and reduce interfacial film viscosity. Petroleum sulfonates have an upper salinity limit of about 2 percent sodium chloride.¹⁰ There are however, numerous chemically floodable reservoirs that were identified in U.S. Department of Energy studies⁹ or in the U.S. Department of Energy TORIS data base of reservoir properties which can be used to identify reservoirs where petroleum sulfonates will work. Historically, petroleum sulfonates have been applied in some reservoirs that had much higher salinity and relied upon a fresh water preflush of the reservoir to reduce the salinity to the level where the petroleum sulfonate was effective.³ To increase the brine tolerance of petroleum sulfonates, ethoxylated alcohols or other cosurfactants have also been incorporated into chemical formulations.¹²⁻¹⁷ Preflushes to change the salinity in corefloods are effective, but this approach has historically proven ineffective in the field.³

Synthetic surfactants such as the ethoxylated sulfonates,¹¹⁻¹² orthoxylene sulfonates,¹⁴⁻¹⁵ or α -olefinsulfonates¹⁶ increase the salinity tolerance but also increase the per pound cost of the surfactant. However, higher cost surfactants can be tolerated if they are cost-effective. As with any surfactant, each has its limitations. Considerable effort has been exerted toward developing these surfactants, defining their phase behavior and conditions of applicability with the goal of improved performance and increased oil recovery. Selection of a surfactant must also be considered are the surfactant feedstock supply, competing markets, the cost of synthesis, and the capabilities of plants to produce the surfactant, because flooding one field may require millions of pounds of surfactant per year for as long as 5 years. Adjacent zones or fields may require just as much, but a totally different surfactant.

Orthoxylenesulfonates,¹⁴⁻¹⁵ or alkylbenzenesulfonates¹⁷⁻¹⁸ can withstand higher salinities and many could be effective at seawater salinity. The recent review by Salter¹⁹ indicates that linear or rod-shaped surfactants have both higher optimal salinities and higher solubilization parameters at optimum conditions. The α -olefinsulfonates can withstand salinities from 5 to 10 percent sodium chloride. The alkylvinylidene sulfonates can withstand higher

salinities but yield low solubilization.²⁰ The branched chain ethoxylated sulfonates can be ethoxylated to yield surfactants that span the salinity range from 0.5 to about 20 percent sodium chloride and have high solubilization parameters.²¹

Carboxylates²² and ethoxylated carboxylates² have been shown to be effective over a wide range of salinities that range from about 0.5 percent sodium chloride for carboxylates to greater than 30 percent sodium chloride for the ethoxylated carboxylates.

Nonionic surfactants are extremely salt tolerant but have received mixed reviews. The problems of high adsorption²³ and low solubilization²⁴ which plagued their applications have been somewhat overcome by better choice of surfactant structure.²⁵

Within recent years, several literature reviews and papers^{3,19,26-34} have indicated different directions for designing cost-effective chemical flooding surfactants. Surfactants are classified as either cationic, amphoteric, anionic or nonionic. The last three classes have the greatest potential in chemical flooding³⁵ because of the negative charge on reservoir rocks. Cationic surfactants which are strongly adsorbed on reservoir rock, because of the rocks negative charge, will have only selected applications in chemical flooding such as in profile modification which uses cationic surfactants to reduce permeability in highly permeable zones. Adsorption, retention, entrapment, precipitation, phase separation, partitioning (all losses of surfactant) are significant and sometimes overwhelming problems for surfactants from the other classes, depending upon the surfactant structure, and the reservoir environment where they are to be applied. Selection of the current surfactants is a critical parameter in ensuring the success of a chemical flood.

Both industrial and academic research have contributed greatly to the development of chemical systems for surfactant flooding as indicated by the thousands of patents and at least an equal number of published papers. Many oil and service companies have developed their own procedures to aid in designing effective flooding systems. Salinity screening, phase behavior screening,^{11,34,36-40} adsorption measurements and laboratory corefloods are the typical sequence of tests for evaluation of a surfactant system. Gogarty²⁶⁻²⁷ and others³³ have emphasized the need for the use of live crudes

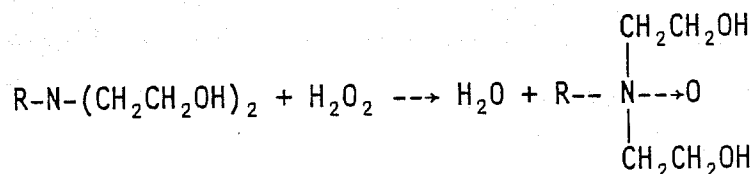
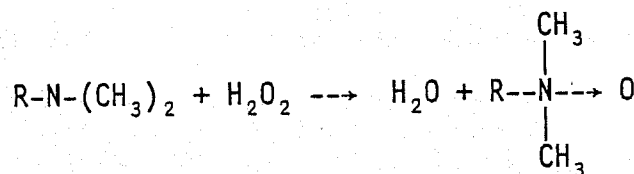
and field cores as soon as possible in the selection and design for a specific reservoir once the surfactant class is chosen.

Based on our literature search, several commercial surfactants were chosen for this study, including carboxymethylated ethoxylates, dinonylphenoethoxy sulfonates and amine oxides. The approach taken was a classical approach of correlation of optimal salinity or phase inversion temperature for a given surfactant (or class of surfactants) with several variables such as alkane carbon number, alcohol type and/or concentration.^{18,34-37}

LABORATORY STUDIES

Amine Oxides

Amine oxides are a class of compounds formed from the oxidation of tertiary amines as shown below for the synthesis from a dimethylalkyltertiary amine and of bis(2-hydroxyethyl)alkyl tertiary amine.⁴¹



The resulting amine oxides have a free electron pair on the nitrogen atom filling the gap in the electron octet of the oxygen atom. The polarity of the semipolar N→O bond in amine oxides is shown schematically either as an arrow or with a positive and negative charge, N⁺-O⁻. The dipole moment of the bond has been calculated as 4.38.⁴²

These surface active compounds are nonionic at the pH of most reservoirs (pH 6 to 8) and become cationic in acid solutions below pH 3. This class of compounds has been used in detergent formulations along with anionic, nonionic, and cationic surfactants. They are used in a wide variety of cosmetic, household, and industrial products because of their foam stabilizing and viscosity building properties. The lower alkyl chain length products

provide foam stabilization properties. They have been used in applications to thicken hydrochloric acid solutions for cleaning formulations. Higher molecular weight in amine oxides provide a "definite softness and conditioning feel" to products such as hair shampoo.⁴³ These materials develop increased viscosity with or without the use of inorganic builders in aqueous solution and are used for this purpose in liquid laundry and hand soaps. They have been promoted as good wetting agents in concentrated electrolyte solutions such as pickling baths for metal plating operations. Formulations containing amine oxides have been used for well workover fluids⁴⁴ and as additives to amine based corrosion inhibitors for downhole applications.

An initial search of the literature indicated only one patent on the use of amine oxides for chemical EOR.⁴⁵ (No displacement tests were reported.) However, during the course of this work a second patent, was filed and assigned to Hoechst A.G.⁴⁶ The initial patent reports only IFT data. The second patent contains both IFT and coreflood data.

There are a number of reasons why amine oxides may have potential as chemical flooding agents:

1. There is at least one patent showing oil recovery.
2. The R groups on the amine provide a wide variety of parameters from which to choose: chain length, branching, ethoxylation in a branch, etc.
3. Amine oxides show good surface tension reductions.
4. These materials demonstrated viscosifying properties, and thus may provide their own mobility control and avoid the use of polymers eliminating surfactant/polymer interaction.
5. A large volume supply is available, though at the current time these are specialty chemicals rather than commodity chemicals.
6. The cost of amine oxides is dependent on the cost of the feedstock,, i.e., palm oil, tallow, etc. and is not petroleum based.

7. There are a large number of manufacturers. The chemistry to produce the end product varies and some manufacturers may have technical advantages in chemistry, plant size, and the active concentration of surfactant solution they can produce, thus avoiding shipping as much as 70 percent non actives (water or alcohol) in their surfactant.

Since most of the amine oxides are derived from natural products, such as coconut or palm oil, rather than polymerization of ethylene or propylene, they will contain a distribution of molecules in the hydrophobe as is shown in table 1. The exception are the products from Ethyl Corporation which are synthesized from ethylene polymerization and contain a narrow product distribution.

Surfactant Composition

Most commercial surfactants are mixtures in the carbon chain length of the hydrophobe, the number of ethylene oxide units incorporated, and the degree of conversion of the nonionic to the anionic surfactant or amine to amine oxide. They may have alcohols or other solvents added for ease in handling.

TABLE 1. - Carbon chain distribution of alcohol ethoxylates^{4 2}

	Coconut	Palm	Hydrogenated tallow	Tallow
<u>Saturated</u>				
C ₈	6			
C ₁₀	7			
C ₁₂	51			
C ₁₄	19	12	3.5	3
C ₁₅		1	0.5	0.5
C ₁₆	9	75	31	29
C ₁₇		1	1	1
C ₁₈	2	11	61	20
<u>Unsaturated</u>				
Tetradecenyl	-	-	-	0.5
Hexadecenyl	-	-	-	2
Octadecenyl	-	-		
Octadecadienyl	-	-	} 3	} 44

Though the amine oxide samples did not contain appreciable amounts of salt, they did contain free amine (less than 2.5 percent) and hydrogen peroxide (less than 0.34 percent). Amine oxide solutions and other surfactants were prepared as concentrates for PIT, viscosity, phase behavior, and screening tests and are on a weight-volume, g/100 ml, basis. The amine oxides were not purified, and the analysis as reported by the manufacturer is shown in table 2. Many of these materials are experimental and will meet requirements of the TSCA Section 5(h) R&D Exemption.

TABLE 2. - Properties of amine oxides under study

Manufacturer	Trade Name	Chemical Structure			AO Active, %	COS, % ¹
		R1	R2	R3		
Armak	Aromox					
	DM16W	Palm	CH ₃	CH ₃	30	
	DM16	Palm	CH ₃	CH ₃	40	IPA, 36
	DMHT	H Tallow	CH ₃	CH ₃	43.4	IPA, 36
	DMMC-W	Coco	CH ₃	CH ₃	30	
	T//12	Tallow	CH ₃	CH ₃	40	IPA, 40
	C/12-W	Coco	CH ₃ CH ₂ OH	CH ₃ CH ₂ OH	40	
Sherex	Varox					
	1770	Coco amido	CH ₃	CH ₃	35±5	
	743	COCO	CH ₃ CH ₂ OH	CH ₃ CH ₂ OH	50±5	IPA, 20±5
	748					
	Varonic T202	Tallow	CH ₃ CH ₂ OH	CH ₃ CH ₂ OH	31.4	
	DP SC 192-103	H Tallow	CH ₃ CH ₂ OH	CH ₃ CH ₂ OH	19.9	
	EP SC 192-15	Coco	Coco	CH ₃	85±10	
Ethyl	EP SC 192-185	C ₈ -C ₁₀	C ₈ -C ₁₀	C ₈ -C ₁₀	90	
		C ₁₄ (98%)	CH ₃ CH ₂ OH	CH ₃ CH ₂ OH	33.9	
		C ₁₀ (82%)	C ₁₀	CH ₃	77.9	
Lonza	Barlox					
	12	Coco	CH ₃	CH ₃	30	
	16S	Cetyl	CH ₃	CH ₃	30	
	18S	Stearyl	CH ₃	CH ₃	25	

¹COS = cosolvent and % by weight, balance is water. IPA = isopropyl alcohol.

Salinity Tolerance

Surfactant solubility was determined in vial tests at two temperatures (ambient and 50° C) and on a range of salinities for a number of amine oxides and sulfonated ethoxylated nonylphenols, to establish an upper salinity and/or hardness tolerance. Test variables include: brine salinity (percent NaCl), hardness tolerance (CaCl₂), combinations of salinity and hardness, surfactant concentration and temperature. The stability (flocculation, precipitation or phase separation) of these formulations were noted by visual inspection at 48 hours. Samples that were soluble were advanced to Phase Inversion Temperatures (PIT) scans, phase behavior or viscosity screening tests.

Viscosity Scans

The viscosity of the surfactant solutions was measured at various temperatures using a Brookfield LVT cone and plate viscometer. Viscosity readings were converted to a shear rate of 12 sec⁻¹ for single point comparison. Viscosities of amine oxides were conducted within 48 hours of mixing and then stored at 50° C for 1 month in sealed vials (no attempt was made to purge oxygen from the solutions before storage), and then viscosity measurements were repeated. The viscosity of a series of freshly prepared dimethylalkylamine oxide are shown in figures 1 and illustrate the range of viscosities that are achievable without the use of polymer. Using a surfactant that can provide mobility control to the surfactant slug would be advantageous although amine oxides would probably not displace polymers in a mobility control slug to chase the surfactant slug because polymers can be applied at 500 to 1,000 ppm to achieve the same viscosity as the amine oxides shown in figure 1. However, a viscosifier that could reduce interfacial tension would be advantageous. An alkyl chain length of at least tetradecyl (C₁₄) is needed in the dimethylalkylamine oxide series to achieve sufficient viscosity for use in chemical flooding.

Amine oxides with ethoxylation incorporated into the molecule such as bis(2-hydroxyethyl)tallowamine oxide (Varonic T202) did not show as much ability to build viscosity. This molecule was the first of a series of ethoxylated tallow amine oxide studied in an attempt to reduce the requirement for alcohols as cosolvents.

Phase Inversion Temperature

The phase inversion temperature, PIT, is the temperature at which a water-in-oil emulsion, which has been stabilized by the surfactant, changes into an oil-in-water emulsion and vice versa.⁴⁵⁻⁴⁸ The process can be easily followed by monitoring the electrical conductivity of a stirred mixture as a function of temperature. At low temperatures, an oil-in-water emulsion of high conductivity is present. As the temperature is raised the electrical conductivity of the brine slowly increases (a positive temperature coefficient is usually observed for electrolytes). At a given point, the electrical conductivity of the mixture decreases, often three or more orders of magnitude. Near this temperature, an onset of schlieren occurs and transparent streaks are visible. Upon further heating the mixture becomes essentially nonconducting and a water-in-oil emulsion is present. Often a color change accompanies this transition: for clear refined oils the mixture becomes white and opaque whereas with black crude oils the emulsion becomes brown, or tan and opaque. Storage of formulations at their PIT temperature often results in multiphase behavior upon standing undisturbed at this temperature.

The correlation of PIT and the conditions for development of three phase microemulsion systems has recently been the subject of a series of papers by Salager:⁴⁹ "...the PIT of the emulsion correlates fairly well with the optimum or HLB-temperature (optimum temperature for three-phase behavior) for three-phase behavior, the former often gives a good estimate of the latter."⁴⁹⁻⁵⁴

PIT measurements were conducted using a Yellow Springs Instrument, model 32 electrical conductivity bridge with a YSI 3403 conductivity electrode modified for increased flow of fluid through the electrode. The test cell was stirred continuously and equipped for operation to 60 psig. A description of the system is found in Department of Energy Report No. NIPER-318.⁵⁵

Figures 2 through 4 illustrate the dependence of PIT on pH, salinity, and alkane carbon chain length for a bis(2-hydroxyethyl)tallow amine oxide (Varonic T202). The PIT decreases and becomes sharper (inverts over a smaller temperature range) with increasing salinity (figure 2), decreases with lower pH (figure 3), and decreases with shorter alkane carbon number (figure 4). The PIT increases as the water solubility of the alcohol increases (no

figure). Preliminary data indicate the sharp drop in electrical conductivity, as shown in figure 4, correlates with variations in the width of the three-phase region observed in both salinity and temperature phase partitioning scans.

Phase Volume Scans

Phase partitioning tests were conducted after temperature selection by PIT experiments. These studies were either a salinity scan to establish the width of the three-phase region or alkane carbon scan. In both procedures solutions were made up at a constant oil/water ratio, 1:1, in disposable 10 ml glass pipets that were sealed and incubated in water baths at the specified temperature.

The equilibration of phase tubes takes from 2 weeks to 6 months. Selection of an approximate salinity or temperature window was reduced by analysis of the PIT data. Table 3 shows the drastic difference changing the alcohol cosolvent can make on the three phase window. The use of isobutyl alcohol and dimethylhydrogenatedtallow amine oxide yields a broad three phase region that covers 9.2 percent NaCl and a high solubilization parameter.

Coreflooding Results

Coreflooding results are shown in table 4 and figure 5 for dimethylhydrogenatedtallow-amine oxide, indicating that in spite of the high solubilization parameter and low interfacial tension between decane and the

TABLE 3. - Phase behavior of dimethylhydrogenatedtallowamine oxide after 2 months of equilibration time versus decane at 50° C

3% surfactant	Salinity range % NaCl	(% NaCl) S^*	Maximum Solubilization parameter
Plus 3% isobutyl alcohol	5.6 to 14.8	8.1	38
Plus 3% isopentyl alcohol	0 to 1.0	0.41	26

TABLE 4. - Coreflood results on 10-in Berea sandstone core using 3% dimethylhydrogenated tallow amine oxide and 3% isobutyl alcohol at 50° C, 8.1% NaCl and decane

Core No.	IFT, mN/m	Surfactant		Biopolymer		Re, ¹ %
		PV, %	VIS, cp	PV, %	VIS, cp	
A01	18	20	2.4	1.5	12	22
A02	18	50	2.4	1.5	12	61
A03	18	100	2.4	0.8	12	78

¹Re = $(S_{ow} - S_{oc}) / S_{ow} \times 100$ (see reference 2).

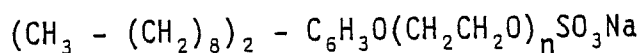
amine oxide-alcohol system the chemical flood was stripping oil rather than banking oil. Oil recovery increases as the quantity of surfactant injected is increased.

Recommendations

Additional work should be pursued to define structure-performance correlations of amine oxides both with alcohols as cosolvents and with ethoxylation and propoxylation incorporated into the molecule. A study is required to resolve why oil was stripped rather than banked in corefloods including detailed analysis of the produced fluids.

Dinonylphenol Ethoxylated Sulfonates

The samples of ethoxylated dinonylphenol(EO)_n sulfonate with n = 3,6,9,



as supplied by GAF Corporation were initially screened as received and later purified⁵⁶ to separate the salt and nonionics from the anionic surfactant of interest. Commercial use of the purified anionic would not be economically feasible since purification may increase the cost as much as five times. On the sample containing an average of three, six, or nine ethylene oxide groups,

good phase behavior (salinity and EACN scans from ambient to 90° C) was not obtained (multiple viscous gel phases appear in solution) without addition of at least equal volume amounts of isobutyl alcohol. Figure 6 shows the PIT's decreasing with increasing salinity for the surfactant formulation of dinonylphenol (EO), sulfonate (1%) and 3% 2-butanol. These systems are salt tolerant but separation of alcohol from the surfactant would be expected to produce gels that would plug pore throats. This defeated the intended purpose of finding cosurfactant-free slugs and therefore further work on the series was not pursued. The research group at the University of Texas, Austin, has recently pursued the phase behavior of the higher ethoxylated molecules in this series and found alcohol addition was required.⁵⁷

Sulfonates Based Upon Ethoxylated Guerbet Alcohols

Henkel Corporation markets a series of Guerbet alcohols under the trade name of "Rilanit G."⁵⁸ These materials are characterized by branching at the position beta to the hydroxyl group. They are easily obtained from the base catalyzed thermal condensation of iso-alcohols. The Guerbet reaction allows the synthesis of selected branched chain, uniform high molecular weight alcohols in high yield. These alcohols are a good source of twin tail surfactants after the alcohol is ethoxylated and converted to the anionic form via sulfonation, sulfation or carboxylation. The study of surfactants based on these alcohols due to the presentation in April 1986 of both the synthesis⁵⁹ and phase behavior⁶⁰ of a series of sulfonates based on ethoxylated Guerbet alcohols by workers at the University of Texas. Twin tail surfactants based upon sulfonated ethoxylated Guerbet showed moderate salinity tolerance and high solubilization parameters without the addition of an alcohol cosolvent.

Carboxymethylated Ethoxylates

Topical report (NIPER-228) entitled "Carboxymethylated Ethoxylated Surfactants"² describes a method of selecting surfactants for chemical enhanced oil recovery using carboxymethylated ethoxylated surfactants (CES). Structure/performance correlations for hydrophobe and ethylene oxide content have been developed for a series of CES with alkane carbon number, pH, salinity, and PIT to provide a guide in selecting candidate surfactants for

enhanced oil recovery. CES are a class of surfactants that generate low IFT (5 to 50 millidyne/cm as observed (against crude oils at high temperature, high salinity and high divalent ion concentration. Selection of the surfactant for a specific reservoir can be made based upon determination of the phase PIT of the surfactant at reservoir salinity and live crude oil. An additional scan for phase behavior (salinity scan) can then establish salinity tolerance and solubilization parameters for the selected surfactant system.

CONCLUSIONS AND SUMMARY

Three classes of surfactants were pursued during our screening of surfactants to design cosurfactant-free chemical flooding systems. NIPER made more progress on defining parameters that effect application of ethoxylated carboxymethylated ethoxylates and started the screening of amine oxides. The latter class of surfactants have now been ethoxylated and/or propoxylated such that they may be cosurfactant alcohol-free chemical flooding agents. The following paragraphs summarize the research results from each of these classes of surfactant.

Dinonylphenol Ethoxylated Sulfonates

The dinonylphenol ethoxy sulfonates require at least an equal volume of alcohol or ethoxylated alcohol (nonionic precursor) and thus these surfactants were not advanced beyond phase partitioning tests. Possibly longer ethylene oxide chains than EO = 9 will reduce the requirement for a cosolvent.

Carboxymethylated Ethoxylates

Carboxymethylated ethoxylates provide surfactants that have a high tolerance to salinity and divalent ions. PIT is one rapid preliminary method for selecting a CES for a specific application. Phase behavior and oil displacement tests in long (i.e., four foot) cores are required to complete the screening. Oil recoveries from the corefloods conducted at NIPER with the nonylphenol CES that were blended for use at the reservoir conditions corresponding to that of North Burbank field were disappointing. Oil recovery was low. Pressure buildup throughout the runs indicate the presence of gels or macroemulsions. The use of PIT alone is not sufficient to select the surfactant but must be combined with phase behavior studies.

Amine Oxides

Phase behavior and viscosity scans of a number of amine oxides have been conducted. Thus far, the dimethylamine oxides are characterized as generating wide three phase microemulsion systems that have high solubilization parameters over a wide salinity window, and they also provide high viscosity without the use of polymer. The amine oxides have thus far required alcohol as cosolvents, although phase behavior studies on fourteen additional ethoxylated and propoxylated amine oxides have been initiated. Results from oil displacement tests indicate stripping of oil rather than formation of an oil bank despite the low interfacial tension.

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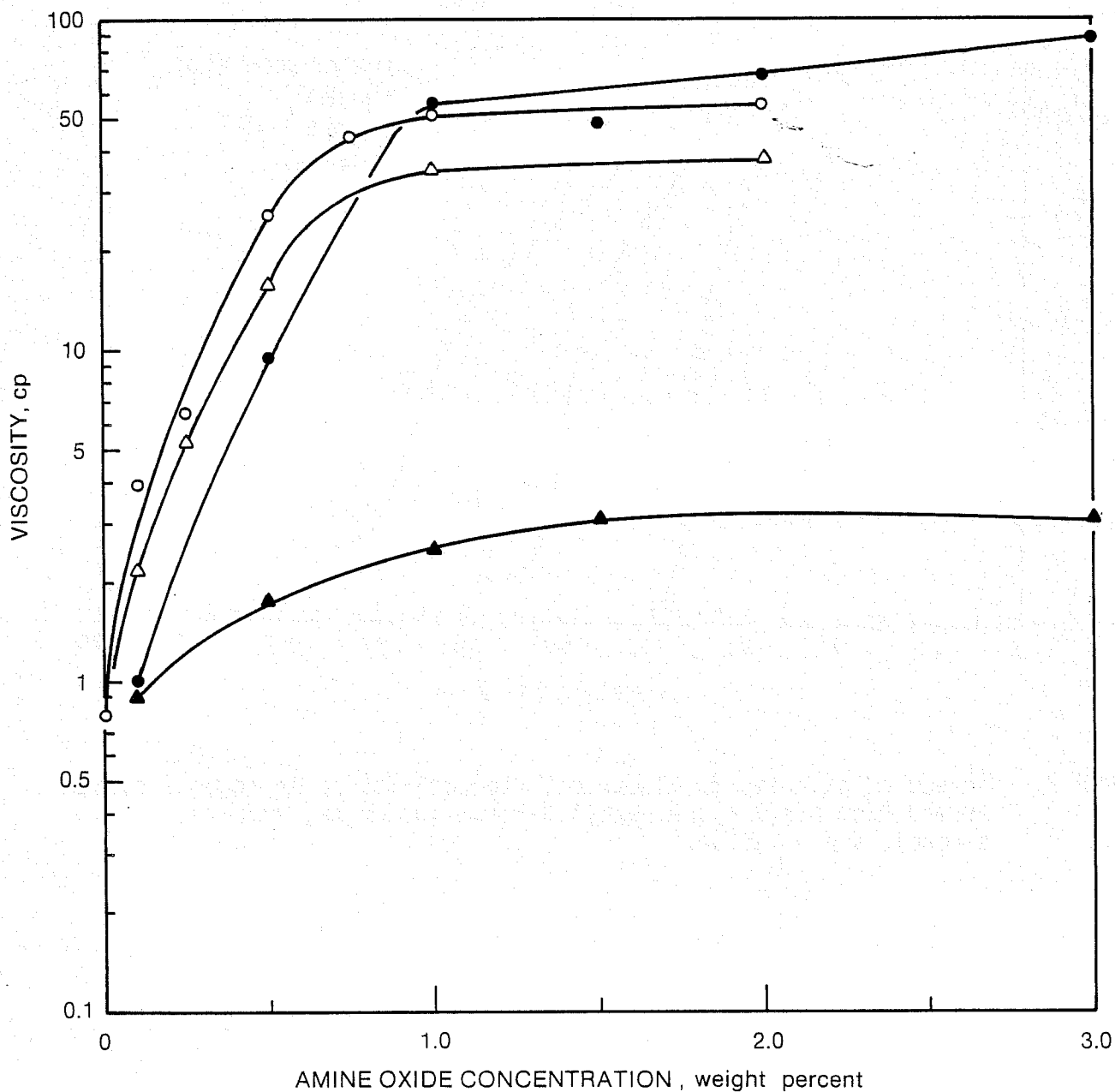


FIGURE 1. - Viscosity of dimethyltallowamine oxide in 0.5% NaCl, ●, dimethyltallowamine oxide in synthetic seawater, ○, dimethylhydrogenatedtallowamine oxide in synthetic seawater, △, bis(2-hydroxyethyl)tallowamine oxide in synthetic seawater, ▲. All viscosity measurements at ambient temperature.

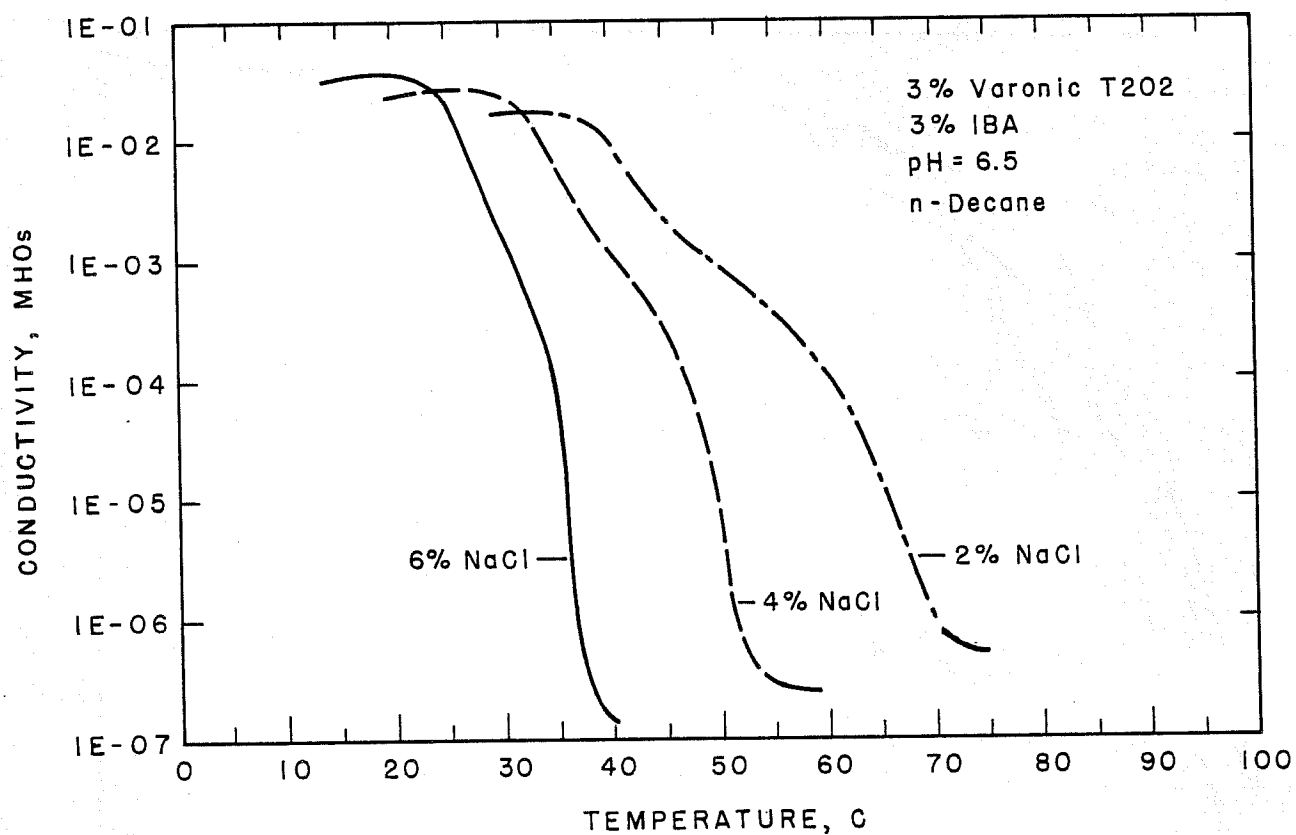


FIGURE 2. - Effect of salinity on electrical conductivity of an aqueous system formed from bis(2-hydroxyethyl)tallowamine oxide, isobutyl alcohol, and n-decane.

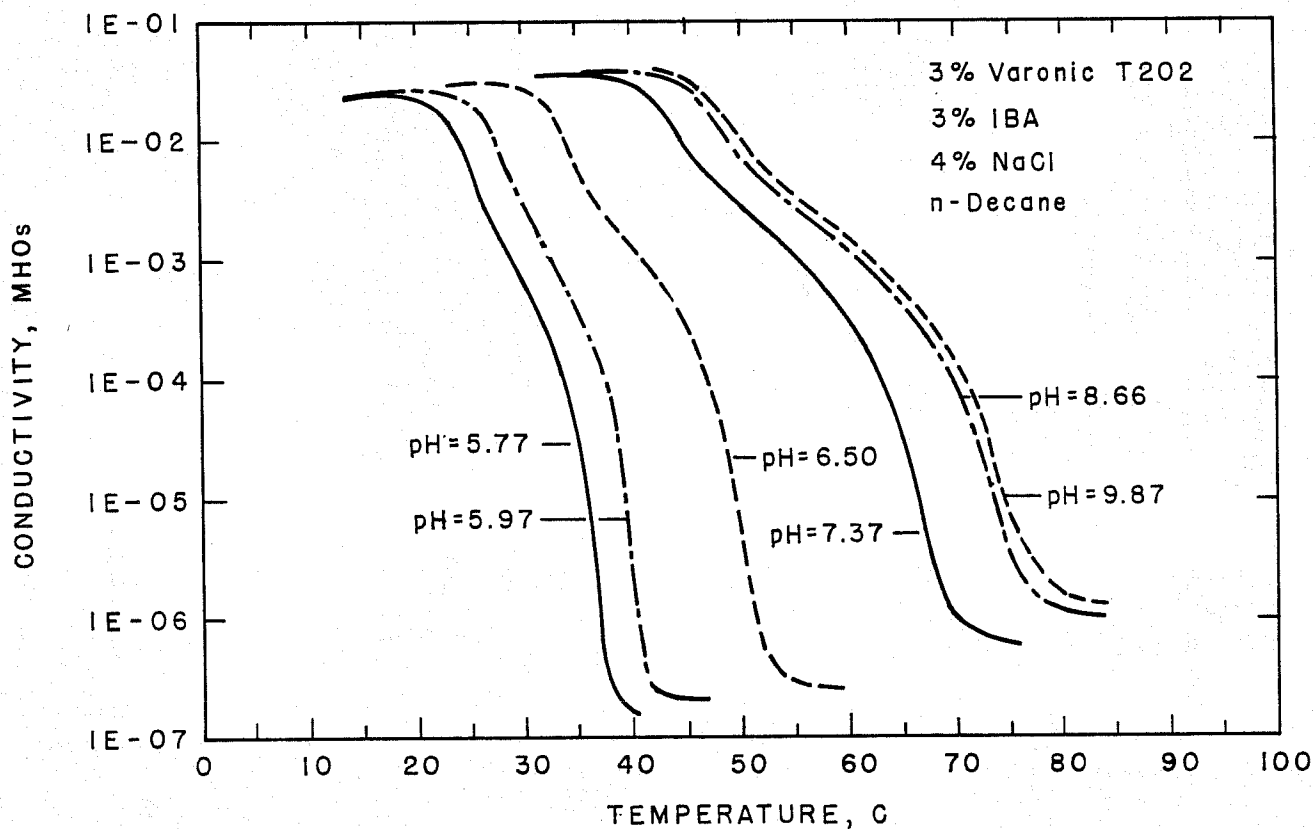


FIGURE 3. - Effect of pH on electrical conductivity of an aqueous system formed from bis(2-hydroxyethyl)tallowamine oxide, isobutyl alcohol, and n-decane.

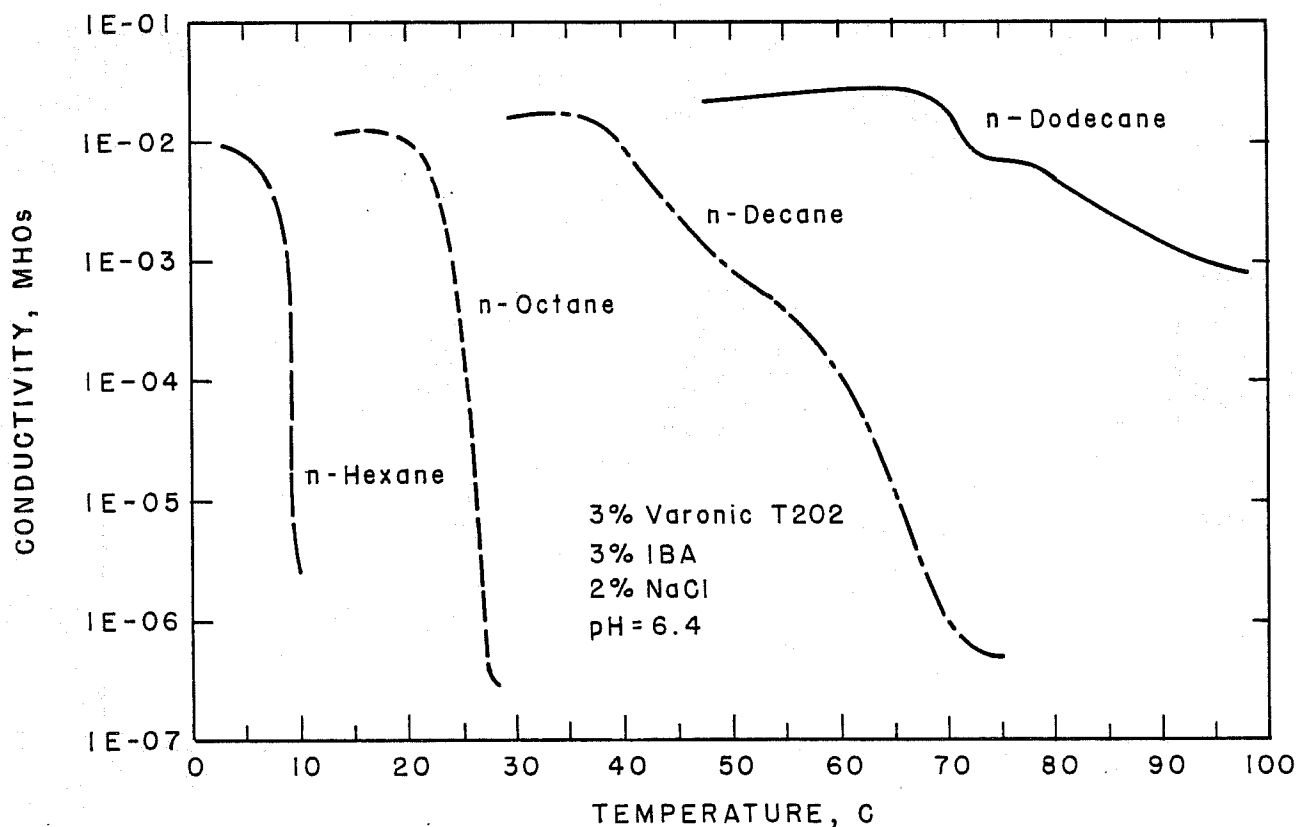


FIGURE 4. - Effect of alkane carbon chain on the electrical conductivity of an emulsion system formed from an aqueous solution bis(2-hydroxyethyl)tallowamine oxide and isobutyl alcohol.

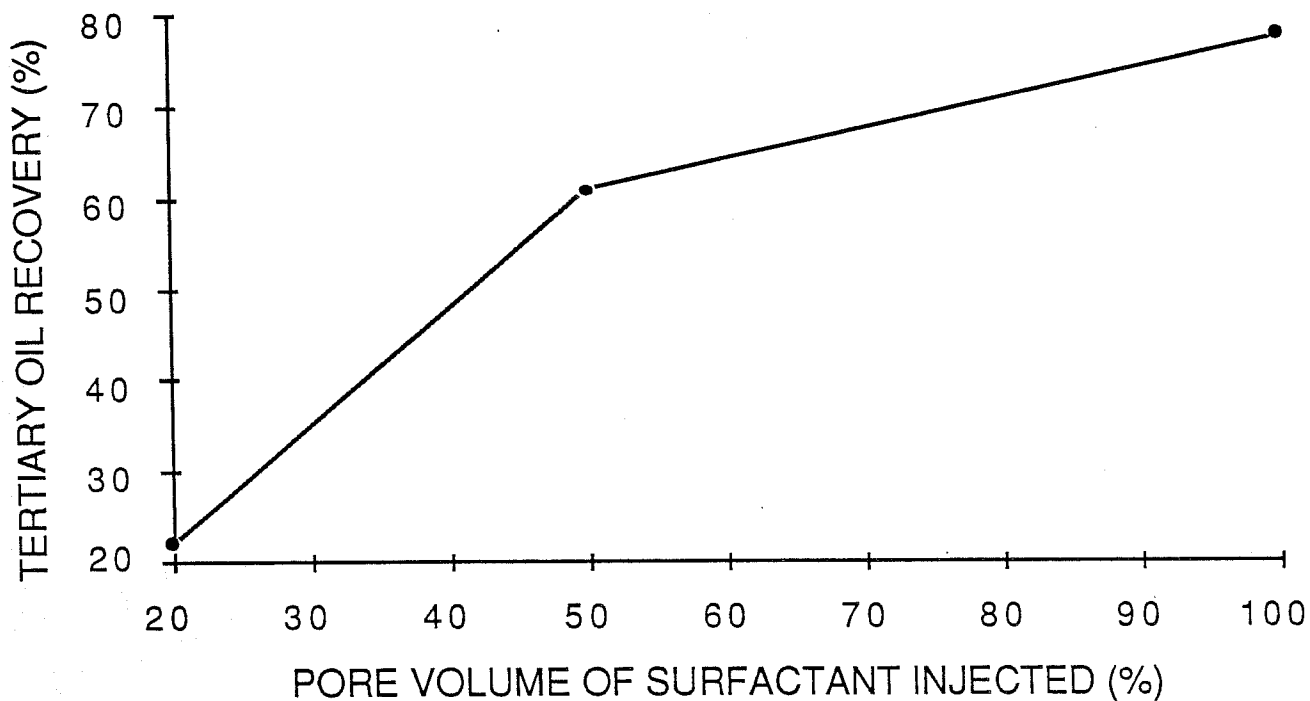


FIGURE 5. - Results of corefloods of decane with a surfactant formulation of 3% dimethylhydrogenatedtallowamine oxide with 3% isobutyl alcohol.

1% DNPS-9E0,3% 2-Butanol, NaCl and n-Decane System

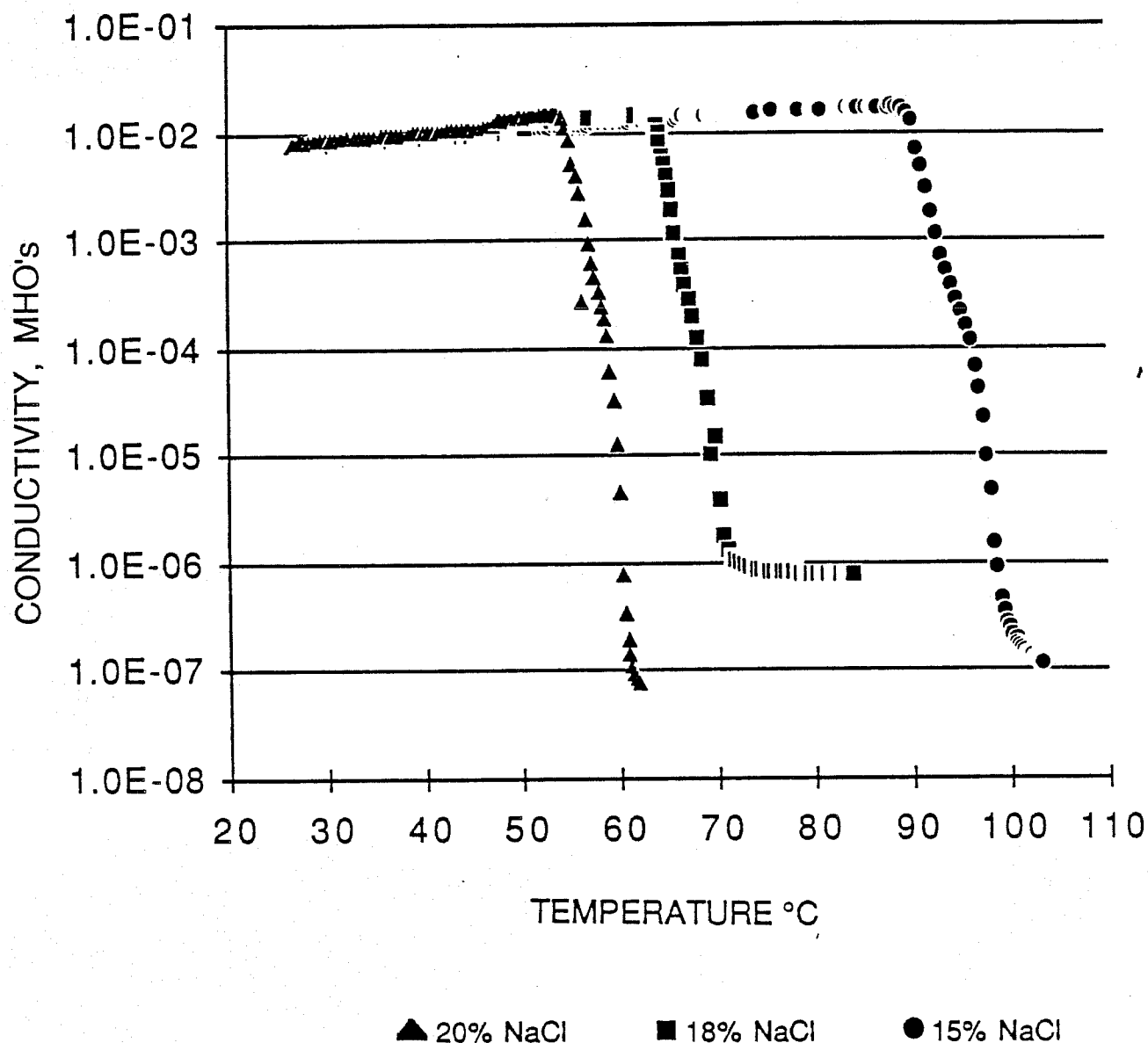


FIGURE 6. - PIT behavior of 1% ethoxylated dinonylphenol sulfonate with nine ethylene oxide groups and 3% 2-butanol with n-decane.

